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(54) **High melt strength, propylene polymer, process for making it, and use thereof**

Propylenpolymer mit hoher Schmelzfestigkeit, Verfahren zu seine Herstellung und seine Verwendung

Polymère de propylène à haute résistance à l'état fondu, procédé de fabrication et utilisation

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Description

This invention resides in the chemical arts. More particularly, it relates to the chemical art having to do with synthetic resins derived from alpha or 1-olefins. Specifically, it relates to impact modified synthetic resins, also known as hetero-

5 ophasic resin, formed by the sequential polymerization of propylene and other olefins.

Radiation of polymer materials as a method of chemical processing is known in the art. For example, Bohm and Tveekrem, "The Radiation Chemistry of Elastomers And Its Industrial Application", Rubber Chemistry and Technology, vol. 55, 575-668, discuss the effect of radiation of elastomers, such as ethylene-propylene copolymers and terpolymers; and Harmer and Ballantine, "Applying Radiation to Chemical Processing", Chemical Engineering, 91-98, May/ 1971

10 which describes various types of radiation.

The irradiation of elastomers, such as ethylene-propylene copolymer rubbers or ethylene-propylene-diene terpolymer rubbers is a viable method, or alternative, for crosslinking said materials, as described in O'Donnell and Whittaker, "The Radiation Crosslinking and Scission of Ethylene-Propylene Copolymers Studied by Solid-state Nuclear Magnetic Resonance", British Polymer Journal, vol. 17, no.1, 51-55, 1985. The crosslinking of elastomers is desirable in fabri-

15 cated parts. U.S. 4,170,664 describes a process for the production of cross-linked resilient automotive body components having a cured surface coating from a thermoplastic elastomeric composition.

It is also known that by irradiating normally solid, linear, C₂₋₄ alpha-olefin homopolymers and random copolymers of propylene with ethylene and/or C₄₋₈ alpha-olefins, according to the processes of U.S. 4,916,198; 5,047,446 and 5,047,485, polymers are obtained having high melt strength or strain hardening (an increased resistance to stretching

20 during elongation of the molten material) without crosslinking and gelation.

However, when irradiated C₂₋₄ alpha-olefin homopolymers and random copolymers of propylene with ethylene and/or C₄₋₈ alpha-olefins are blended with irradiated or non-irradiated elastomers to obtain better impact strength, the melt strength suffers.

The irradiation of heterophasic resins by conventional radiation methods has resulted in an heterophasic resin

25 having melt strength, but severe gelation and high degree of crosslinking, which are undesirable in foam applications. Thus, there is a need for high rubber heterophasic resins having good melt strength without substantial gelation or high degree of crosslinking.

This invention in one aspect comprises an irradiated normally solid, high molecular weight, non-linear, substantially gel-free, propylene polymer material being obtainable by a process comprising

30 (1) irradiating a normally solid, high molecular weight, linear, propylene polymer material (a) without strain hardening elongational viscosity, in an environment in which the active oxygen concentration is established and maintained at less than about 15% by volume of said environment (b) with high energy ionizing radiation at a dose rate in the range from about 1 to about 1x10⁴ megarads per minute for a period of time sufficient for a substantial

35 amount of chain scission of the linear, propylene polymer to occur, but insufficient to cause gelation of the material;

(2) maintaining the thus irradiated material in such an environment for a period of up to one hour; and

40 (3) then treating the irradiated material while in such an environment to deactivate substantially all the free radicals present in the irradiated material,

wherein the molecular chains of said propylene polymer material have a substantial amount of free-end long branches, a significant strain hardening elongational viscosity and enhanced melt strength, selected from the group consisting essentially of:

45 (1) a propylene polymer composition consisting essentially of:

(a) from 10 to 50% of a propylene homopolymer having an isotactic index of from 80 to 99%, or a copolymer selected from the group consisting of (i) propylene and ethylene, (ii) propylene, ethylene and a CH₂=CHR alpha-olefin, where R is a C₂₋₈ straight or branched alkyl, and (iii) propylene and an alpha-olefin, as defined above in (a) (ii), wherein said copolymer contains from 85 to 99% propylene and having an isotactic index greater than 80 to 99%,

50 (b) from 5 to 20% of a semi-crystalline, essentially linear copolymer fraction having a crystallinity of 20 to 60%, by differential scanning calorimetry (DSC), wherein the copolymer is selected from the group consisting of (i) ethylene and propylene containing over 55% ethylene; (ii) ethylene, propylene, and an alpha-olefin, as defined above in (a) (ii), containing from 1 to 10% of the alpha-olefin and over 55% up to 98% of both ethylene and alpha-olefin; and (iii) ethylene and an alpha-olefin, as defined in (a) (ii), containing over 55% up to 98% of said

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alpha-olefin, which copolymer is insoluble in xylene at room or ambient temperature, and

(c) from 40 to 80% of a copolymer fraction selected from the group consisting of a copolymer of (i) ethylene and propylene wherein the copolymer contains from 20% to less than 40% ethylene; (ii) ethylene, propylene, and an alpha-olefin, as defined in (a) (ii), wherein the alpha-olefin is present in an amount of from 1 to 10% and the amount of ethylene and alpha-olefin present is from 20% to less than 40%; and (iii) ethylene and an alpha-olefin, as defined in (a) (ii), containing from 20 to less than 40% of the alpha-olefin, and optionally containing 0.5 to 10% of a diene, said copolymer fraction being soluble in xylene at ambient temperature, and having an intrinsic viscosity preferably of from 1.7. to 3.0 dl/g, wherein the total amount of ethylene units or said alpha-olefin units or of ethylene and said alpha-olefin units when both are present in the composition is from 15 to 35%, the total amount of (b) and (c) fractions, based on the total olefin polymer composition is from 65% to 80%, the weight ratio of (b)/(c) is preferably from 0.1 to about 0.3 and the total content of ethylene or C₄₋₈ alpha-olefin or combination thereof in (b+c) is less than 50%; and

(2) a propylene polymer composition consisting essentially of:

(a) 10-60 parts by weight of homopolymer polypropylene with isotactic index greater than 90 to 99, or of crystalline propylene copolymer with ethylene, with a CH₂=CHR olefin where R is a 2-6 carbon alkyl radical, or combinations thereof, containing over 85% by weight of propylene and having an isotactic index greater than 85 to 94%;

(b) 8-40 parts by weight of a crystalline, polymer fraction containing ethylene and propylene, having an ethylene content greater than 50% and insoluble in xylene at room temperature;

(c) 30-60 parts by weight of an amorphous ethylene-propylene copolymer fraction containing optionally small proportions of a diene, soluble in xylene at room temperature and containing 40 to 70% by weight ethylene.

This invention in another aspect provides a practical process for converting normally solid, high molecular weight, linear, propylene polymer material without strain hardening elongational viscosity into irradiated normally solid, high molecular weight, non-linear, substantially gel-free, propylene polymer material, that has significant strain hardening elongational viscosity and enhanced melt strength comprising:

(1) irradiating said linear, propylene polymer material (a) in an environment in which the active oxygen concentration is established and maintained at less than 15% by volume of said environment (b) with high energy ionizing radiation at a dose rate in the range from 1 to 1x10⁴ megarads per minute for a period of time sufficient for a substantial amount of chain scission of the linear, propylene polymer to occur, but insufficient to cause gelation of the material;

(2) maintaining the thus irradiated material in such an environment for a period of up to one hour; and

(3) then treating the irradiated material while in such an environment to deactivate substantially all the free radicals present in the irradiated material,

wherein said propylene polymer material of the present invention is a normally solid, high molecular weight, non-linear, substantially gel-free propylene polymer material of:

(1) a propylene polymer composition consisting essentially of:

(a) from 10 to 50% of a propylene homopolymer, preferably from 10 to 40%, and most preferably from 20 to 35%, having an isotactic index of from 80 to 99%, and preferably from 85 to 99%, or a copolymer selected from the group consisting of (i) propylene and ethylene, (ii) propylene, ethylene and a CH₂=CHR alpha-olefin, where R is a C₂₋₈ straight or branched alkyl, and (iii) propylene and an alpha-olefin, as defined above in (a) (ii), wherein said copolymer contains from 85 to 99%, and preferably from 90 to 97% propylene and having an isotactic index greater than 80 to 99%, preferably greater than 85 to 98%,

(b) from 5 to 20% of a semi-crystalline, essentially linear copolymer fraction, preferably from 7 to 15%, having a crystallinity of 20 to 60%, by differential scanning calorimetry (DSC), wherein the copolymer is selected from the group consisting of (i) ethylene and propylene containing over 55% ethylene; (ii) ethylene, propylene, and an alpha-olefin, as defined above in (a)(ii), containing from 1 to 10% of the alpha-olefin and over 55% up to

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98%, preferably from 80 to 95%, of both ethylene and alpha-olefin; and (iii) ethylene and an alpha-olefin, as defined in (a)(ii), containing over 55% up to 98%, preferably from 80 to 95%, of said alpha-olefin, which copolymer is insoluble in xylene at room or ambient temperature, and

(c) from 40 to 80% of a copolymer fraction, preferably 50 to 70%, selected from the group consisting of a copolymer of (i) ethylene and propylene wherein the copolymer contains from 20% to less than 40%, preferably from 20 to 38%, most preferably 25 to 38% ethylene; (ii) ethylene, propylene, and an alpha-olefin, as defined in (a)(ii), wherein the alpha-olefin is present in an amount of from 1 to 10%, preferably from 1 to 5%, and the amount of ethylene and alpha-olefin present is from 20% to less than 40%; and (iii) ethylene and an alpha-olefin, as defined in (a)(ii), containing from 20 to less than 40%, preferably 20 to 38%, and most preferably 25 to 38% of the alpha-olefin, and optionally containing 0.5 to 10%, preferably 1 to 5% of a diene, said copolymer fraction being soluble in xylene at ambient temperature, and having an intrinsic viscosity preferably of from 1.7 to 3.0 dl/g, wherein the total amount of ethylene units or said alpha-olefin units or of ethylene and said alpha-olefin units when both are present in the composition is from 15 to 35%, the total amount of (b) and (c) fractions, based on the total olefin polymer composition is preferably from about 65% to 80%, the weight ratio of (b)/(c) is preferably from 0.1 to about 0.3 and the total content of ethylene or C₄₋₈ alpha-olefin or combination thereof in (b+c) is less than 50%, and preferably from 20 to 45%; or

(2) a propylene polymer composition consist essentially of:

(a) 10-60 parts by weight of homopolymer polypropylene with isotactic index greater than 90 to about 99%, or of crystalline propylene copolymer with ethylene, with a CH₂=CHR olefin where R is a 2-6 carbon alkyl radical, or combinations thereof, containing over 85% by weight of propylene and having an isotactic index greater than 85 to 99%;

(b) 8-40 parts by weight of a crystalline, polymer fraction containing ethylene and propylene, having an ethylene content greater than 50%, preferably from 50 to 99%, and insoluble in xylene at room temperature;

(c) 30-60 parts by weight of an amorphous ethylene-propylene copolymer fraction containing optionally small proportions of a diene, soluble in xylene at room temperature and containing 40 to 70% by weight ethylene.

All parts and percentages used in this application are by weight unless otherwise specified. Ambient or room temperature is approximately 25°C.

The propylene polymer material treated according to the process of this invention is a normally solid, high molecular weight, linear, propylene polymer material selected from the group consisting essentially of:

(1) a propylene polymer composition consisting essentially of:

(a) from 10 to 50% of a propylene homopolymer, preferably from 10 to 40%, and most preferably from 20 to 35%, having an isotactic index of from 80 to 99 %, and preferably from 85 to 99%, or a copolymer selected from the group consisting of (i) propylene and ethylene, (ii) propylene, ethylene and a CH₂=CHR alpha-olefin, where R is a C₂₋₈ straight or branched alkyl, and (iii) propylene and an alpha-olefin, as defined above in (a)(ii), wherein said copolymer contains from 85 to 99%, and preferably from 90 to 97% propylene and having an isotactic index greater than 80 to 99%, preferably greater than 85 to 98%,

(b) from 5 to 20% of a semi-crystalline, essentially linear copolymer fraction, preferably from 7 to 15%, having a crystallinity of 20 to 60%, by differential scanning calorimetry (DSC), wherein the copolymer is selected from the group consisting of (i) ethylene and propylene containing over 55% ethylene; (ii) ethylene, propylene, and an alpha-olefin, as defined above in (a)(ii), containing from 1 to 10% of the alpha-olefin and over 55% up to 98%, preferably from 80 to 95%, of both ethylene and alpha-olefin; and (iii) ethylene and an alpha-olefin, as defined in (a)(ii), containing over 55% up to 98%, preferably from 80 to 95%, of said alpha-olefin, which copolymer is insoluble in xylene at room or ambient temperature, and

(c) from 40 to 80% of a copolymer fraction, preferably 50 to 70%, selected from the group consisting of a copolymer of (i) ethylene and propylene wherein the copolymer contains from 20% to less than 40%, preferably from 20 to 38%, most preferably 25 to 38% ethylene; (ii) ethylene, propylene, and an alpha-olefin, as defined in (a)(ii), wherein the alpha-olefin is present in an amount of from 1 to 10%, preferably from 1 to 5%, and the amount of ethylene and alpha-olefin present is from 20% to less than 40%; and (iii) ethylene and an alpha-olefin, as defined in (a)(ii), containing from 20 to less than 40%, preferably 20 to 38%, and most preferably 25 to 38% of the alpha-olefin, and optionally containing 0.5 to 10%, preferably 1 to 5% of a diene, said copolymer fraction being soluble in xylene at ambient temperature, and having an intrinsic viscosity preferably of from 1.7 to 3.0 dl/g, wherein the total amount of ethylene units or said alpha-olefin units or of ethylene and said

alpha-olefin units when both are present in the composition is from 15 to 35%, the total amount of (b) and (c) fractions, based on the total olefin polymer composition is preferably from 65% to 80%, the weight ratio of (b)/(c) is preferably from 0.1 to about 0.3 and the total content of ethylene or C₄₋₈ alpha-olefin or combination thereof in (b+c) is less than 50%, and preferably from 20 to 45%, having at least one melt peak, determined by DSC, present at temperatures higher than 120°C, and at least one peak, relative to the vitreous transition, present at temperatures from -10°C and -35°C. In addition, these compositions have a flexural modulus of less than 150 MPa, generally from 20 and 100 MPa; a tensile strength at yield of from 10 to 20 MPa, elongation at break over 400%; a tension set, at 75% strain, from 20% to 50%; a Shore D hardness from 20 and 35; haze value of less than 40%, preferably less than 35%, and do not break (no brittle impact failure) when an IZOD impact test is conducted at -50°C.; and

(2) a propylene polymer composition consisting essentially of:

(a) 10-60 parts by weight of homopolymer polypropylene with isotactic index greater than 90 to about 99%, or of crystalline propylene copolymer with ethylene, with a CH₂=CHR olefin where R is a 2-6 carbon alkyl radical, or combinations thereof, containing over 85% by weight of propylene and having an isotactic index greater than 85 to 99%;

(b) 8-40 parts by weight of a crystalline, polymer fraction containing ethylene and propylene, having an ethylene content of greater than 50%, preferably from 50 to 99% and insoluble in xylene at room temperature;

(c) 30-60 parts by weight of an amorphous ethylene-propylene copolymer fraction containing optionally small proportions of a diene, soluble in xylene at room temperature and containing 40 to 70% by weight ethylene, having at least one melting peak, determined by DSC, present at temperatures higher than 140°C; a flex modulus of less than 700 MPa, preferably from 200 to 500 MPa; a VICAT softening point greater than 50°C; a Shore A hardness greater than 80 and a Shore D hardness greater than 30; a tension set, at 75% strain, lower than 60%, and preferably from 20 to 50%; a tensile stress of greater than 6 MPa, and preferably from 8 to 20 MPa and a notched Izod resilience at -20° and -40°C greater than 600 J/m.

The high molecular weight, linear, propylene polymer material treated according to the process of this invention under the broadest concepts of the process can be in any physical form, for example, spherical, granules, pellets, film and sheet. However, in preferred embodiments of the process of this invention, the linear, propylene polymer material is in a finely divided condition with satisfactory results being obtained at an average spherical or pellet particle size of 0.5 to 7mm.

As used herein, "high molecular weight" means weight average molecular weight of at least 100,000.

Intrinsic viscosity, also known as the limiting viscosity number, in its most general sense is a measure of the capacity of a polymer molecule to enhance the viscosity of a solution. This depends on both the size and the shape of the dissolved polymer molecule. Hence, in comparing a nonlinear polymer with a linear polymer of substantially the same weight average molecular weight, it is an indication of configuration of the nonlinear polymer molecule. Indeed, the above ratio of intrinsic viscosities is a measure of the degree of branching of the nonlinear polymer. A method for determining intrinsic viscosity of propylene polymer material is described by Elliott et al., J. App. Poly. Sci., 14, pp 2947-2963 (1970). In this specification the intrinsic viscosity in each instance is determined with the polymer dissolved in decahydronaphthalene at 135°C.

Melt tension provides an indicator of the melt strength of the material. Melt tension is determined with a Gottfert Rheotens melt tension apparatus from Gottfert Inc. by measuring the tension of a strand of molten polymer material in centi-newtons as follows: the polymer to be examined is extruded at an extrusion rate of 0.13 cc/sec. at an apparent shear rate of approximately 15 reciprocal seconds and temperature of from 140°C to 200°C through a capillary 20 mm long and 2 mm in diameter; the strand is then subjected to stretching using a drawing system with a constant acceleration rate based on the particular material. The tension resulting from the above drawing is measured (in centi-newtons). The higher the melt tension means the greater the melt strength values which, in turn, are indicative of the particular material's strain hardening ability.

Elongational viscosity is the resistance of a fluid or semifluid substance to elongation. It is a melt property of a thermoplastic material, that can be determined by an instrument that measures the stress and strain of a specimen in the melt state when subjected to tensile strain at a constant rate. One such instrument is described in, and shown in Fig. 1 of, Munstedt, J. Rheology, 23, (4), 421-425, (1979). A commercial instrument of similar design is the Rheometrics RER-9000 extensional rheometer. Molten, high molecular weight, linear, propylene polymer material exhibits elongational viscosity which, as it is elongated or drawn at a constant rate from a relatively fixed point, tends to increase for a distance dependent on the rate of elongation, and then to decrease rapidly until it thins to nothing - so-called ductile or necking failure. On the other hand, the molten propylene polymer material of this invention, that is of substantially the same weight average molecular weight and at substantially the same test temperature as the corresponding, molten,

high molecular weight, linear, propylene polymer material, exhibits elongational viscosity which, as it is elongated or drawn from a relatively fixed point at substantially the same rate of elongation tends to increase over a longer distance, and it breaks or fails by fracture - so-called brittle or elastic failure. These characteristics are indicative of strain hardening. Indeed, the more long chain branching the propylene polymer material of this invention has the greater the tendency of the elongational viscosity to increase as the elongated material approaches failure. This latter tendency is most evident when the branching index is less than 0.8.

The stretch recovery or tension set of the material of this invention is a measure of the materials elasticity. Stretch recovery is determined by measuring the permanent deformation in a molded sample elongated to high deformation on a tensile testing instrument and then allowed to relax for a preset period of time. For the purpose of this invention, stretch recovery is defined as the permanent deformation, measured after 30 minutes, in a specimen elongated to break at a cross head speed of 50,8 cm/min (20 in./min at room temperature. It can be expressed as a percent permanent deformation relative to the original gauge length of the undeformed specimen or as a percent of break elongation of the material.

Because the irradiation results in chain scission, even though there is recombination of chain fragments to reform chains, as well as joining of chain fragments to chains to form branches, there can be a net reduction in weight average molecular weight between the starting material and the end product, the desired substantially branched, high molecular weight, non-linear, propylene polymer material. In general, the intrinsic viscosity of the starting, linear, propylene polymer material, which is indicative of its molecular weight, should be in general 1-25, and preferably 2-6, to result in an end product with an intrinsic viscosity of 0.8-25, and preferably 1-3. However, linear, propylene polymer material with intrinsic viscosities higher and lower than these general values are within the broader scope of this invention.

The active oxygen content of the environment in which the three process steps are carried out is a critical factor. The expression "active oxygen" herein means oxygen in a form that will react with the irradiated material and more particularly the free radicals in the material. It includes molecular oxygen (which is the form of oxygen normally found in air). The active oxygen content requirement of the process of this invention can be achieved by use of vacuum or by replacing part or all of air in the environment by an inert gas such as, for example, nitrogen.

Linear, propylene polymer material immediately after it is made is normally substantially free of active oxygen. Therefore, it is within the concepts of this invention to follow the polymerization and polymer work-up steps (when the propylene polymer material is not exposed to air) with the process of this invention. However, in most situations the linear, propylene polymer material will have an active oxygen content because of having been stored in air, or for some other reason. Consequently, in the preferred practice of the process of this invention the linear, propylene polymer material is first treated to reduce its active oxygen content. A preferred way of doing this is to introduce the material into a bed of the same blown with nitrogen, the active oxygen content of which is equal to or less than 0.004% by volume. The residence time of the material in the bed generally should be at least 5 minutes for effective removal of active oxygen from the interstices of the particles of the material, and preferably long enough for the material to be in equilibrium with the environment.

Between this preparation step and the irradiation step, the prepared, linear, propylene polymer material should be maintained in an environment in which the active oxygen concentration is less than 15%, preferably less than 5% in a gas conveyance system, and more preferably 0.004%, by volume of the environment. In addition, temperature of the linear, propylene polymer material should be kept above the glass transition temperature of the amorphous fraction of the material, generally at less than 40°C and preferably at 25°C, because of the increase in temperature of the material that occurs in the irradiation step.

In the irradiation step the active oxygen concentration of the environment preferably is less than 5% by volume, and more preferably less than 1% by volume. The most preferred concentration of active oxygen is 0.004% by volume.

In the irradiation step, the ionizing radiation should have sufficient energy to penetrate to the extent desired the mass of linear, propylene polymer material being radiated. The energy must be sufficient to ionize the molecular structure and to excite atomic structure, but not sufficient to affect atomic nuclei. The ionizing radiation can be of any kind, but the most practical kinds comprise electrons and gamma rays. Preferred are electrons beamed from an electron generator having an accelerating potential of 500-4,000 kilovolts. In the case of propylene polymer material without a polymerized diene content, satisfactory results are obtained at a dose of ionizing radiation of 0.5-7 megarads, preferably 2-6 megarads, delivered generally at a dose rate of 1-10,000 megarads per minute, and preferably 18-2,000 megarads per minute. In the case of propylene polymer material having a polymerized diene content, satisfactory results are obtained with a dose of 0.20 to 2.0 megarads, preferably 0.5 to 1.5 megarads, delivered at the foregoing dose rates.

The term "rad" is usually defined as that quantity of ionizing radiation that results in the absorption of 100 ergs of energy per gram of irradiated material, regardless of the source of radiation. As far as the instant invention is concerned, the amount of energy absorbed by the propylene polymer material when it is irradiated usually is not determined. However, in the usual practice of the process energy absorption from ionizing radiation is measured by the well known conventional dosimeter, a measuring device in which a strip of fabric containing a radiation sensitive dye is the energy absorption sensing means. Hence, as used in this specification the term "rad" means that quantity of ionizing radiation

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resulting in the absorption of the equivalent of 100 ergs of energy per gram of the fabric of a dosimeter placed at the surface of the propylene polymer material being irradiated, whether in the form of a bed or layer of particles, or a film, or a sheet.

5 The second step of the process of this invention should be performed in a period of time generally in the range from one minute to one hour, and preferably 2-30 minutes. A minimum time is needed for sufficient migration of propylene polymer chain fragments to free radical sites and for combination thereof to reform complete chains, or to form long branches on chains. A radical migration time less than one minute, for example, a half minute, is within the broader concepts of this invention, but is not preferred because the amount of resulting free-end long chain branching is quite low.

10 The final step of the process, the free radical deactivation or quenching step, can be performed by the application of heat or by the addition of an additive that functions as a free radical trap, such as, for example, methyl mercaptan.

In one embodiment of the process the application of heat comprises extruding the irradiated propylene polymer material at about 200°C. At this temperature the irradiated propylene polymer material is melted. As a result, quenching of the free radicals is substantially complete. In this embodiment, prior to the extrusion or melt compounding, the irradiated propylene polymer material can be blended with other polymers, for example, linear, propylene polymer material, if desired, and additives such as, for example, stabilizers, pigments and fillers. Alternatively, such additives can be incorporated as a side stream addition to the extruder.

15 In another embodiment of the inventive process the application of heat is achieved by introducing the irradiated propylene polymer material into a fluidized bed or a staged fluid bed system in which the fluidizing medium is, for example, nitrogen or other inert gas. The bed or beds is or are established and maintained in a temperature range of at least 60°C up to 130°C and preferably 80-120°C, with the average residence time of the irradiated propylene polymer material in the fluid bed or beds being from 5 minutes to 120 minutes, with 20-30 minutes being optimum.

The product thus obtained is a normally solid, high molecular weight, non-linear, substantially gel-free, propylene polymer material characterized by strain hardening and enhanced melt strength.

25 By "substantially gel-free", as used herein, it is meant that the gel content of the material is from 0 to less than 3%.

Although the process of the invention can be carried out on a batch basis, preferably it is performed on a continuous basis. In one continuous embodiment of the process the finely divided, linear, propylene polymer material, either with or without the preparation step, depending on the active oxygen content of the material, is layered on a traveling belt in the required environment. The thickness of the layer depends on the desired extent of penetration of the ionizing radiation into the layer and the proportion of linear, propylene polymer material desired in the final end product. The speed of travel of the traveling belt is selected so that the layer of finely divided, propylene polymer material passes through the beam or beams of ionizing radiation at a rate to receive the desired dose of ionizing radiation. After having received the desired dose of ionizing radiation, the irradiated layer can be left on the traveling belt in said environment for the period of time for free-radical migration and combination to occur, and then removed from the belt, and introduced into an extruder operated at a melt temperature of the irradiated material, or, in another specific embodiment introduced into a heated bed, or a staged system of heated beds, of particles of irradiated material fluidized with nitrogen or other inert gas. In either embodiment, the irradiated material after at least substantially all of the free radicals therein are deactivated is discharged into the atmosphere and quickly cooled to room temperature. In another embodiment, the irradiated, propylene polymer material is discharged from the belt and conveyed in the required environment to a holding vessel, the interior of which has the required environment, and held in the vessel to complete the requisite free radical migration time. The irradiated material then is introduced into an extruder operated at a melt temperature of the irradiated material or is introduced into a heated, inert gas fluidized bed, or a staged system of fluidized beds, of irradiated particles of propylene polymer material and, after quenching of the free radicals, the irradiated propylene polymer material is discharged into the atmosphere.

45 This invention in still another aspect comprises the extensional flow use of the strain hardening, propylene polymer material of this invention. Extensional flow occurs when the propylene polymer material in the molten condition is pulled in one or more directions at a rate faster than it would normally flow in those directions. It happens in extrusion coating operations in which a melted coating material is extruded on to a substrate such as a moving web of paper or metal sheet, and the extruder or substrate is moving at a higher rate than the extrusion rate. It takes place in film production when the molten film is extruded and then stretched to the desired thinness. It is present in thermoforming operations in which a molten sheet is clamped over a plug mold, vacuum is applied and the sheet is pushed into the mold. It occurs in the manufacture of foamed articles, such as sheets, beads, cups and plates, in which molten propylene polymer material is expanded with a foaming agent. The strain hardening propylene polymer material of this invention is particularly useful as part of (for example from as little as 0.5% by weight to as much as 95% or more by weight) or as substantially all of the molten plastic material used in these and other melt processing methods (for example, profile extrusion, as in the melt spinning of fibers) for making useful articles. In the case of the strain hardened propylene polymer material of this invention, it is particularly useful when blended with a normally solid, predominantly isotactic, semi-crystalline, linear, propylene polymer material for use in melt processing and other operations for making useful

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articles.

This invention is further illustrated by the accompanying drawings which form a material part of these disclosures, and by the following examples.

Fig. 1 is a schematic flow sheet of a preferred embodiment of a continuous process for converting, for example, normally solid, linear propylene polymer material into a normally solid, non-linear, substantially gel-free, propylene polymer material with strain hardening and enhanced melt strength.

Fig. 2 is a schematic flow sheet of a preferred embodiment of a continuous process for converting, for example, normally solid, linear propylene polymer material into a normally solid, non-linear, substantially gel-free, propylene polymer material with strain hardening and enhanced melt strength, without the additive hopper 37, screw feeder 38, bulk feed hopper 41 and screw feeder 42.

In greater detail, Fig. 1 depicts a fluid bed unit 10 of conventional construction and operation into which finely divided, high molecular weight, propylene polymer material is introduced by way of conduit 11, nitrogen gas is introduced by way of conduit 13, and from which substantially active oxygen free, high molecular weight, propylene polymer material is removed by way of a solids discharge conduit 15 which also has a solids flow rate controller 16. The solids discharge conduit 15 leads to a conveyer belt feed hopper 20.

The conveyer belt feed hopper 20 is a capped structure of conventional design. It is operated so that its interior contains a nitrogen atmosphere. It has a bottom solids discharge outlet through which the propylene polymer material particles move and form a layer on the top horizontal run of an endless conveyer belt 21.

The conveyer belt 21 is generally horizontally disposed, and continuously moves under normal operative conditions. It is contained in radiation chamber 22. This chamber completely encloses the conveyer belt, and is constructed and operated to establish and maintain a nitrogen atmosphere in its interior.

In combination with the radiation chamber 22 is an electron beam generator 25 of conventional design and operation. Under normal operative conditions it generates a beam of high energy electrons directed to the layer of propylene polymer material particles on the conveyer belt 21. Below the discharge end of the conveyer belt is a solids collector 28 arranged to receive the irradiated propylene polymer material particles falling off the conveyer belt 21 as it turns into its path of opposite travel. Irradiated propylene polymer material particles in the solids collector 28 are removed therefrom by a rotary valve or star wheel 29 and delivered thereby to a solids transfer line 30.

The transfer line 30 leads to a gas-solids separator 31. This unit is of conventional construction and usually is a cyclone type separator. Gas separated therein is removed as by gas discharge conduit 33 while separated solids are discharged therefrom as by a rotary valve or star wheel 32 into a solids discharge line 34. The solids discharge line 34 can lead directly to an extruder hopper 35. However, in the embodiment shown, it leads to a plow blender 36.

In the embodiment shown, there is provided a hopper 37 for such additives as stabilizers or an additive concentrate consisting essentially of finely divided linear polypropylene (or even the polypropylene or other high melt strength, propylene polymer material of this invention) and additives at greater concentrations than in the final product. The additive hopper 37 preferably is conventional, and preferably is constructed and operated to maintain the contents in a nitrogen atmosphere. The discharge end of the additives hopper 37 empties into a screw feeder 38 which feeds material into an additives transfer line 39 that goes to the plow blender 36. In addition, in the embodiment shown, there is provided a bulk feed hopper 41 in which, for example, finely divided or pelletized linear polypropylene is contained. This hopper is conventional, and it too preferably is constructed and operated to maintain the contents in a nitrogen atmosphere. The bulk feed hopper 41 empties into a screw feeder 42 which feeds a solids transfer line 43 that goes to the plow blender 36. In the plow blender 36, the solids fed into it are blended and then discharged into a blended feed line 45 that empties into the extruder hopper 35.

The extruder hopper 35, which feeds an extruder 47, is conventional in construction and operation. It too is an enclosed structure adapted for establishing and maintaining a nitrogen atmosphere in its interior. The extruder 47 is of conventional construction, and is operated in normal fashion. The solids in the extruder hopper 35 move therefrom into the extruder which is operated at a rate of extrusion to result in the period of time between irradiation of the propylene polymer material and its entry into the extruder being sufficient for a significant amount of free-end, long chain branches to form. Accordingly, the volume of the extruder hopper 35 is selected to provide, if necessary, the desired amount of hopper storage time to meet this condition. The extruder 47 is designed (length of extruder barrel and screw) and operated at a melt temperature and at a pressure sufficient to maintain the free radical containing propylene polymer material therein for the amount of time needed to deactivate substantially all of the free radicals present.

The thus treated, propylene polymer material is characterized by being non-linear, substantially gel-free, and substantially branched with free-end long chains of propylene polymer units. It can be used as is, or introduced, for example, directly into a pelletizing and cooling unit 49 and conveyed away therefrom as by solids transport line 50 as solid pellets which can be stored and then used, or used without storage.

Similar results are achieved when other specific embodiments of linear, high molecular weight, propylene polymer material are treated according to the continuous process just depicted.

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The following examples illustrate the high molecular weight, non-linear, substantially gel-free, propylene polymer material of this invention, and the foregoing preferred embodiment of a process for making it.

The test samples and physical properties of the following working examples and comparative examples were prepared and measured according to the following methods:

Melt Flow Rate (MFR)	ASTM D-1238, Condition L
Tensile Strength	ASTM-D 638
Weldline Strength (W.L.)	ASTM-D 638, Dual Gated Tensile bar
Retained Weldline Strength	ASTM-D 638
Elongation @ Break	ASTM-D 638
Elongation @ Yield	ASTM-D 638
Elongation @ Break at W.L.	ASTM-D 638
Flexural Modulus	ASTM-D 790
Flexural Strength	ASTM-D 618, Procedure A
Haze %	ASTM-D 1003
Notched Izod (J/m (ft lb/in))	ASTM-D 256-87

The percent gel is determined by a hot-gel filtration test, whereby the polymer is dissolved in a 1% xylene solution at 135°C and is filtered through a 325 mesh stainless steel screen.

The percent xylene solubles at room temperature, (XSRT), is determined by dissolving 2.5 g of the polymer in 250 ml of xylene in a vessel equipped with a stirrer which is heated at 135°C with agitation for 20 minutes. The solution is cooled to 25°C while continuing the agitation, and then left to stand without agitation for 30 minutes so that the solids can settle. The solids are filtered with filter paper, the remaining solution is evaporated by treating it with a nitrogen stream, and the solid residue is vacuum dried at 80°C until constant weight is reached.

Example 1

A propylene polymer material, in spherical form, containing 35% of a propylene-ethylene copolymer, (3.3 wt.% polymerized ethylene units), and 65% of an ethylene-propylene copolymer, (71 wt.% polymerized ethylene units), having a MFR of 0.98 dg/min., XSRT of 61.7%, and % gel of 0.1, is tumble blended with 0.12% of B225 stabilizer is extruded on a Haake twin screw extruder at 150 rpm and 232°C (450°F), pelletized, and introduced into the fluid bed unit 10 and fluidized with nitrogen for 60 minutes.

The thus treated propylene polymer material is then dropped into the conveyer belt feed hopper 20 which lays it on the moving conveyer belt 21 to form a bed of propylene polymer material 1.5 cm high and 6.25 cm wide. The bed is passed by the conveyer belt 21 through an electron beam generated by a 2 MeV Van de Graff generator operating at a 80 μamp beam current. The conveyor belt speed was adjusted to result in an absorbed surface dose of 2 Mrad. In addition, the active oxygen content of the environment or atmosphere within the enclosed radiation chamber 22 and in the remaining part of the system comprising the irradiated propylene polymer transfer line 30, the solids-gas separator 31, the separator discharge line 34, and the extruder hopper 35, is established and maintained at less than 40 ppm.

After irradiation, the propylene polymer material falls off the end of the conveyer belt 21 into the belt discharge collector 28 and through the rotary valve 29 into the transfer line 30. After separation of gas from the irradiated polymer, the polymer is fed through the separator discharge line 34 into the extruder hopper 35.

The extruder 47 is a 1.87 cm barrel diameter single screw Brabender extruder operated at a 195°C and 180 rpm. The extruded strands of product from the die are cooled in water and then cold sliced to form pellets.

The pellets were then stabilized with 0.07% PEPQ stabilizer, 0.07% Irganox 1010 2,2-bis[[3-[3,5-bis(1,1-dimethylethyl)-4-hydroxyphenyl]-1-oxopropoxy]methyl]-1,3-propanediyl-3,5-bis-(1,1-dimethylethyl)-4-hydroxybenzenepropanoate stabilizer, and 0.25% DSTDP stabilizer. The mixture was then molded on a 42.5 g (1.5 oz.) Battenfeld injection molding machine at 246°C (475°F) and mold temperature of 57°C (135°F).

Properties of the end product of Example 1 are summarized in the following Table I.

Control 1

A propylene polymer material, in spherical form, containing 35% of a propylene-ethylene copolymer, (3.3 wt.% polymerized ethylene units), and 65% of an ethylene-propylene copolymer, (71 wt.% polymerized ethylene units), having a MFR of 0.98 dg/min., XSRT of 61.7%, and % gel of 0.1, is tumble blended with 0.12% of Irganox B 225 2,2-Bis[[3-[3,5-Bis(1,1-dimethylethyl)-4-hydroxyphenyl]-1-oxopropoxy]methyl]-1,3-propanediyl-3,5-Bis(1,1-dimethyl-ethyl)-

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4-hydroxybenzenepropanoate stabilizer and tris(2,4-di-tert-butylphenyl) phosphite stabilizer in a 50:50 blend is extruded on a Haakw twin screw extruder at 150 rpm and 232°C (450°F) and pelletized. The pelletized propylene polymer material was then tumble blended with 0.07% PEPQ stabilizer, 0.07% Irganox 1010 2,2-bis[[3-[3,5-bis(1,1-dimethylethyl)-4-hydroxyphenyl]-1-oxopropoxy]methyl]-1,3-propanediyl-3,5-bis-(1,1-dimethylethyl)-4-hydroxybenzenepropanoate stabilizer, and 0.25% DSTDP stabilizer. The mixture was then molded on a 42,5 g (1.5 oz.) Battenfeld injection molding machine at 246°C (475°F) and mold temperature of 57°C (135°F).

Example 2

Propylene polymer material of the present invention was prepared according to the process set forth in Example 1, except that the bed is passed by the conveyer belt 21 through an electron beam generated by a 2 MeV Van de Graff generator operating at a 230 μamp beam current, instead of 80 μamp; the conveyor belt speed was adjusted to result in an absorbed surface dose of 6 Mrad, instead of 2 Mrad; and the single screw Brabender extruder operated at a 210°C and 180 rpm, instead of 195°C as in example 1.

Example 3

Propylene polymer material of the present invention was prepared according to the process set forth in Example 2, except that the propylene polymer material was not pelletized prior to irradiation, but remained in spherical form; the bed is 1.6 cm high, instead of 1.5 cm high, and the single screw Brabender extruder operated at a 200°C and 180 rpm, instead of 210°C as in Example 2.

Control 2

The propylene polymer material of Example 3 in spherical form, except it has no stabilizers and is not irradiated or extruded.

Example 4

A propylene polymer material, in spherical form, containing 40% propylene homopolymer, 40% ethylene-propylene copolymer rubber and 20% semi-crystalline, ethylene-propylene copolymer fraction which is insoluble in xylene at room temperature and an ethylene content of 96%, having a MFR of 0.75 dg/min., XSRT of 40.0%, and % gel of 0.1, is tumble blended with 0.12% of B225 stabilizer, is extruded in a Haake twin screw extruder at 150 rpm and 232°C (450°F), pelletized, and introduced into the fluid bed unit 10 and fluidized with nitrogen for 60 minutes.

The thus treated propylene polymer material is then dropped onto the conveyer belt feed hopper 20 which lays it on the moving conveyer belt 21 to form a bed of propylene polymer material 1.5 cm high and 6.25 cm wide. The bed is passed by the conveyer belt 21 through an electron beam generated by a 2 MeV Van de Graff generator operating at a 230 μamp beam current. The conveyor belt speed was adjusted to result in an absorbed surface dose of 6 Mrad. In addition, the active oxygen content of the environment or atmosphere within the enclosed radiation chamber 22 and in the remaining part of the system comprising the irradiated propylene polymer transfer line 30, the solids-gas separator 31, the separator discharge line 34, and the extruder hopper 35, is established and maintained at less than 40 ppm.

After irradiation, the propylene polymer material falls off the end of the conveyer belt 21 into the belt discharge collector 28 and through the rotary valve 29 into the transfer line 30. After separation of gas from the irradiated polymer, the polymer is fed through the separator discharge line 34 into the extruder hopper 35.

The extruder 47 is a 1.87 cm barrel diameter single screw Brabender extruder operated at 232°C and 180 rpm. The extruded strands of product from the die are cooled in water and then cold sliced to form pellets.

The pellets were then stabilized with 0.07% PEPQ stabilizer, 0.07% Irganox 1010 2,2-bis[[3-[3,5-bis(1,1-dimethylethyl)-4-hydroxyphenyl]-1-oxopropoxy]methyl]-1,3-propanediyl-3,5-bis-(1,1-dimethylethyl)-4-hydroxybenzenepropanoate stabilizer, and 0.25% DSTDP stabilizer. The mixture was then molded on a 42,5 g (1.5 oz.) Battenfeld injection molding machine at 246°C (475°F) and mold temperature of 57°C (135°F).

The properties of the end product are summarized in Table 1.

Control 3

The propylene polymer material of Example 4, except it is not irradiated. The properties are set forth below in Table 1.

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TABLE 1

	CON* 1	EX 1	EX 2	CON* 2	EX 3	CON* 3	EX 4
5 Dose (Mrad)	0	2	6	0	6	0	6
% EPR	65	65	65	65	65	40	40
10 Tc, Nucleation Temperature (°C)	97.9	99	102.8	98.2	108.7	118.2	121.4
Notched IZOD J/m (ft. lb/in)	293,7 (5.5)	267,0 (5)	304,4 (5.7)	-	-	560,7 (10.5)	512,6 (9.6)
15 Mode of Break	NO BRK	NO BRK	NO BRK	-	-	NO BRK	NO BRK
20 Tensile Strength Yield g/cm ² (psi)	55748 (793)	49772 (708)	48718 (693)	-	-	95327 (1356)	84641 (1204)
25 Weldline Strength g/cm ² (psi)	48226 (686)	46609 (663)	46890 (667)	-	-	70089 (997)	74167 (1055)
Retained Strength (%)	86.5	93.6	96.2	-	-	73.5	87.6
30 Elongation at Yield (%)	28.9	30.2	29.0	-	-	31.3	29.6
Elongation to Break (%)	1146	1100	1100	-	-	1008	960
35 Elongation to Break @ W. L. (%)	1145	1068	841	-	-	19.3	57.2
Flex Modulus kg/cm ² (Kpsi)	1265 (18.0)	1047 (14.9)	998 (14.2)	-	-	4091 (58.2)	3473 (49.4)
40 Flex Strength g/cm ² (psi)	65168 (927)	55537 (790)	54272 (772)	-	-	126470 (1799)	110582 (1573)
M.F.R.	0.98	1.3	1.1	0.8	0.2	0.75	0.3
Melt Tension (cN)	6.1	7.1	16.0	-	22.3	-	-
45 Haze (%)	29	-	21	-	-	-	-
XSRT (%)	61.7	54.6	39.7	67.3	45.8	40.0	22.3
% GEL	0.1	0.3	0.2	0.1	2.6	0.1	1.0

* CON = CONTROL

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It can be seen in Table 1 that Examples 1-4 of the present invention have improved weldline strength, retained strength, and melt tension, with little or no change in tensile strength @ yield, as compared to Controls 1-3, which were not irradiated.

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Examples 5-12 and Controls 4 and 5

A propylene polymer composition, in spherical form, containing (a) 40% propylene homopolymer, (b) 40% ethylene-

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propylene copolymer rubber and (c) 20% semi-crystalline, ethylene-propylene copolymer fraction which is insoluble in xylene at room temperature and having an ethylene content of 96%, a MFR of 0.75 dg/min., XSRT of 40.0%, and % gel of 0.1, is tumble blended with 0.12% of B225 stabilizer is extruded on a Haake twin screw extruder at 150 rpm 232°C (450°F), pelletized and introduced into the fluid bed unit 10 and fluidized with nitrogen for 60 minutes.

The thus treated propylene polymer material is then dropped onto the conveyer belt feed hopper 20 which lays it on the moving conveyer belt 21 to form a bed of propylene polymer material 1.5 cm high and 15 cm wide. The bed is passed by the conveyer belt 21 through an electron beam generated by a 2 MeV Van de Graff generator operating at a 230 μ amp beam current. The conveyor belt speed was adjusted to result in an absorbed surface dose of 1 Mrad. In addition, the active oxygen content of the environment or atmosphere within the enclosed radiation chamber 22 and in the remaining part of the system comprising the irradiated propylene polymer transfer line 30, the solids-gas separator 31, the separator discharge line 34, the blender 36, the blender discharge line 45 and the extruder hopper 35, is established and maintained at less than 40 ppm.

After irradiation, the propylene polymer material falls off the end of the conveyer belt 21 into the belt discharge collector 28 and through the rotary valve 29 into the transfer line 30. After separation of gas from the irradiated polymer, the polymer is fed through the separator discharge line 34 into the blender 36. In these examples, a finely divided additive concentrate, consisting essentially of a linear polypropylene (100 parts by weight), conventional phenolic anti-oxidant (10.1 parts by weight), and calcium stearate (7.0 parts by weight), from the additive hopper 37 is added by way of the additives transfer line 39 to the blender 36 at a rate of 3 parts by weight per 100 parts of the irradiated polymer. The resulting blend is then fed by way of the blender discharge line 45 from the blender 36 into the extruder feed hopper 35.

The extruder 47 is a 6.4 cm barrel diameter single screw Sterling extruder operated at a 240°C and 180 rpm. The extruded strands of product from the die are cooled in water and then cold sliced to form pellets.

Properties of the end products of Examples 5-12 and those of Controls 4 and 5, a non-irradiated polymer described above, are summarized in the following Table 2.

TABLE 2

						Tension Set After Break 20*/min; ~ 30 min Relaxation	
	Dose (Mrad)	%O ₂	MFR (I ₂ @ 230°C)	Tensile Str. @ Break g/ cm ²	Elongation @ Break	% Permanent Deformation	Permanent Deformation as a % of Break Elongation
CON 4	0	40 ppm	0.95	113535 (1615 psi)	285%	135	47
EX 5	1	40 ppm	0.19	115292 (1640 psi)	224%	72	32
EX 6	2	40 ppm	0.12	131883 (1876 psi)	148%	40	27
EX 7	3	40 ppm	0.08	138421 (1969 psi)	135%	33	24
EX 8	5	40 ppm	0.07	130055 (1850 psi)	87%	17	19
CON 5	0	2%	0.94	112339 (1598 psi)	262%	116	45
EX 9	1	2%	0.31	108614 (1545 psi)	241%	89	36
EX 10	2	2%	0.22	122252 (1739 psi)	172%	52	30
EX 11	3	2%	0.28	125204 (1781 psi)	158%	45	28

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TABLE 2 (continued)

	Dose (Mrad)	%O ₂	MFR (I ₂ @ 230°C)	Tensile Str. @ Break g/cm ²	Elongation @ Break	Tension Set After Break 20"/min; ~ 30 min Relaxation	
						% Permanent Deformation	Permanent Deformation as a % of Break Elongation
EX 12	5	2%	0.37	120705 (1717 psi)	102%	25	25

As demonstrated above in Table 2, Examples 5-12 have better tensile strength @ break and higher elastic recovery than Controls 4 and 5.

Controls 6-8

Profax 7901 polypropylene impact modified with 12% ethylene-propylene copolymer rubber having an over all ethylene content of 7.8% was irradiated at various dose levels according to the radiation method described above.

TABLE 3

	CON 6	EX 1	CON 7	EX 2	EX 4	CON 8
Dose (Mrad)	3	2	4.5	6	6	6
% Gel	2.5	0.3	4.4	0.2	1.0	5.3

It can be seen in Table 3 that Examples 1, 2 and 4, all heterophasic resins of the present invention, have lower gel contents than the heterophasics of Control 6, 7 and 8, relative to the radiation dose. This is totally unexpected since the heterophasic resins of the present invention have a higher rubber content, 65%, 65% and 40%, respectively, than the heterophasic of Control 6, 7 and 8, which have 12% rubber.

Example 13 and 14

This example illustrates the use of a propylene polymer material of the present invention in a foam application. The composition of this example contained the product of Example 2 of the present invention.

Tumble blended were 30% of the product of Example 2, 70% of an irradiated propylene homopolymer having a MFR of 3-5, melt strength of 16-18 Cn, XSRT of 4-4.5%, 0.20 pph mineral oil and 0.75 pph of Vertal 350 talc (nucleating agent) before processing. Downstream of the hopper CFC 114 chlorofluorocarbon blowing agent (B.A.) was pumped into the molten mixture at two different levels, (60 and 80% pump stroke that corresponds to 6 and 8% wt. of the blowing agent).

The processing conditions are set forth in Table 4 and the foam performance data are set forth in Table 5.

Table 4

Extruder Temperatures °C (°F)				Adaptor °C (°F)	Die °C (°F)	Melt Temp. °C (°F)	Melt Pressure		Blowing Ing. P. g/cm ² (psi)	Agent Pump stroke (%)
1	2	3	4				Adaptor g/cm ² (psi)	Die g/cm ² (psi)		
191 (375)	207 (405)	191 (375)	163 (325)	154 (310)	149 (300)	160 (320)	70300 (1000)	14060 (200)	45695 (650)	(60,80)

Table 5

	B.A. Level %	MFR %	DENSITY g/cm ³ (lb/ft ³)	NUMBER OF CELLS
Example 13	(6%)	2.76	0,136 (8.49)	10-11
Example 14	(8%)	2.76	0,106 (6.64)	9-10

It can be seen that the blend shows good processability and foam performance, with good foam density and cell structure.

Hence, the propylene polymer material of this invention has utility in melt processing operations to form useful articles, such as foam sheet, for use in any applications where foam sheet materials are employed, such as foam cushioning or packaging and foam beads.

The propylene polymer material also can be used for other applications, such as thermoforming, melt extrusion, sheet extrusion and coextrusion. Indeed, the strain hardening propylene polymer material of this invention is useful in all melt processing operations in which a high molecular weight, propylene polymer material of enhanced melt strength is desired.

Other features, advantages and embodiments of the invention disclosed herein will be readily apparent to those exercising ordinary skill after reading the foregoing disclosures. In this regard, while specific embodiments of the invention have been described in considerable detail, variations and modifications of these embodiments can be effected without departing from the spirit and scope of the invention as described and claimed.

The expression "consisting essentially of" as used in this specification excludes an unrecited substance at a concentration sufficient to substantially adversely affect the essential properties and characteristics of the composition of the matter being defined, while permitting the presence of one or more unrecited substances at concentrations insufficient to substantially adversely affect said essential properties and characteristics.

Claims

1. An irradiated normally solid, high molecular weight, non-linear, substantially gel-free, propylene polymer material being obtainable by the process of claim 5 and having a substantial amount of free-end long branches, a strain hardening elongational viscosity and enhanced melt strength comprising

(1) a propylene polymer composition consisting essentially of:

(a) from 10 to 50% of a propylene homopolymer having an isotactic index of from 80 to 99%, or a copolymer selected from the group consisting of (i) propylene and ethylene, (ii) propylene, ethylene and a $\text{CH}_2=\text{CHR}$ alphaolefin, where R is a C_{2-8} straight or branched alkyl, and (iii) propylene and an alpha-olefin, as defined above in (a) (ii), wherein said copolymer contains from 85 to 99% propylene and having an isotactic index greater than 80 to 99%,

(b) from 5 to 20% of a semi-crystalline, essentially linear copolymer fraction having a crystallinity of 20 to 60%, by differential scanning calorimetry (DSC), wherein the copolymer is selected from the group consisting of (i) ethylene and propylene containing over 55% ethylene; (ii) ethylene, propylene, and an alphaolefin, as defined above in (a) (ii), containing from 1 to 10% of the alpha-olefin and over 55% up to 98% of both ethylene and alpha-olefin; and (iii) ethylene and an alpha-olefin, as defined in (a) (ii), containing over 55% up to 98% of said alpha-olefin, which copolymer is insoluble in xylene at room or ambient temperature, and

(c) from 40 to 80% of a copolymer fraction selected from the group consisting of a copolymer of (i) ethylene and propylene wherein the copolymer contains from 20% to less than 40% ethylene; (ii) ethylene, propylene, and an alpha-olefin, as defined in (a) (ii), wherein the alpha-olefin is present in an amount of from 1 to 10% and the amount of ethylene an alpha-olefin present is from 20%

to less than 40%; and (iii) ethylene and an alpha-olefin, as defined in (a)(ii), containing from 20 to less than 40% of the alpha-olefin, and optionally containing 0.5 to 10% of a diene, said copolymer fraction being soluble in xylene at ambient temperature, and having an intrinsic viscosity of from 1.7 to 3.0 dl/g, wherein the total amount of ethylene units or said alpha-olefin units or of ethylene and said alpha-olefin units when both are

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present in the composition is from 15 to 35%, the weight ratio of (b)/(c) is from 0.1 to about 0.3 and the total content of ethylene or C₄₋₈ alpha-olefin or combination thereof in (b+c) is less than 50%; or
(2) a propylene polymer composition consisting essentially of:

- 5 (a) 10-60 parts by weight of homopolymer polypropylene with isotactic index greater than 90 to 99, or of crystalline propylene copolymer with ethylene, with a CH₂=CHR olefin where R is a 2-6 carbon alkyl radical, or combinations thereof, containing over 85% by weight of propylene and having an isotactic index greater than 85 to 94%;
- 10 (b) 8-40 parts by weight of a crystalline, polymer fraction containing ethylene and propylene, having an ethylene content greater than 50% and insoluble in xylene at room temperature;
- (c) 30-60 parts by weight of an amorphous ethylenepropylene copolymer fraction containing optionally small proportions of a diene, soluble in xylene at room temperature and containing 40 to 70% by weight ethylene.

- 15 2. The propylene polymer material of claim 1, wherein the total amount of (b) and (c) fractions based on the total olefin polymer composition is from 65% to 80%
3. The propylene polymer material of claim 1, wherein component (1) (a) is a copolymer of propylene and ethylene containing from 85 to 99% propylene.
- 20 4. The propylene polymer material of claim 1, wherein component (2) (a) is a polypropylene homopolymer.
5. A process for making irradiated, normally solid, high molecular weight, non-linear, substantially gel-free, propylene polymer material with strain hardening elongational viscosity from normally solid, high molecular weight, linear propylene polymer material without strain hardening elongational viscosity, which comprises:

(1) irradiating said linear propylene polymer material:

- 30 (a) in an environment in which the active oxygen concentration is established and maintained at less than 15% by volume of said environment;
- (b) with high energy ionizing radiation at a dose rate in the range from 1 to 1 x 10⁴ megarads, preferably 18-2,000 megarads, per minute for a period of time sufficient for a substantial amount of chain scission of the linear propylene polymer to occur, but insufficient to cause gelation of the material;

- 35 (2) maintaining the thus irradiated material in such an environment for a period of up to one hour; and
- (3) then treating the irradiated material while in such environment to deactivate substantially all of the free radicals present in the irradiated material,

in which said irradiated normally solid,
40 high molecular weight, non-linear, substantially gel-free, propylene polymer material is

(1) a propylene polymer composition consisting essentially of:

- 45 (a) from 10 to 50% of a propylene homopolymer having an isotactic index of from 80 to 99%, or a copolymer selected from the group consisting of (i) propylene and ethylene, (ii) propylene, ethylene and a CH₂=CHR alpha-olefin, where R is a C₂₋₈ straight or branched alkyl, and (iii) propylene and an alpha-olefin, as defined above in (a)(ii), wherein said copolymer contains from 85 to 99% propylene and having an isotactic index greater than 80 to 99%;
- 50 (b) from 5 to 20% of a semi-crystalline, essentially linear copolymer fraction having a crystallinity of 20 to 60%, by differential scanning calorimetry (DSC), wherein the copolymer is selected from the group consisting of (i) ethylene and propylene containing over 55% ethylene; (ii) ethylene, propylene, and an alpha-olefin, as defined above in (a) (ii), containing from 1 to 10% of the alpha-olefin and over 55% up to 98% of both ethylene and alpha-olefin; and (iii) ethylene and an alpha-olefin, as defined in (a)(ii), containing over 55% up to 98% of said alpha-olefin, which copolymer is insoluble in xylene at room or ambient temperature, and
- 55 (c) from 40 to 80% of a copolymer fraction selected from the group consisting of a copolymer of (i) ethylene and propylene wherein the copolymer contains from 20% to less than 40% ethylene; (ii) ethylene, propylene, and an alpha-olefin, as defined in (a)(ii), wherein the alpha-olefin is present in an amount of from 1

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to 10% and the amount of ethylene and alpha-olefin present is from 20% to less than 40%; and (iii) ethylene and an alpha-olefin, as defined in (a)(ii), containing from 20 to less than 40% of the alpha-olefin, and optionally containing 0.5 to 10% of a diene, said copolymer fraction being soluble in xylene at ambient temperature, and having an intrinsic viscosity of from 1.7 to 3.0 dl/g, wherein the total amount of ethylene units or said alpha-olefin units or of ethylene and said alpha-olefin units when both are present in the composition is from 15 to 35%, the weight ratio of (b)/(c) is from 0.1 to about 0.3 and the total content of ethylene or C₄₋₈ alpha-olefin or combination thereof in (b+c) is less than 50%; or

(2) a propylene polymer composition consisting essentially of:

(a) 10-60 parts by weight of homopolymer polypropylene with isotactic index greater than 90 to 99, or of crystalline propylene copolymer with ethylene, with a CH₂=CHR olefin where R is a 2-6 carbon alkyl radical, or combinations thereof, containing over 85% by weight of propylene and having an isotactic index greater than 85 to 94%;

(b) 8-40 parts by weight of a crystalline, polymer fraction containing ethylene and propylene, having an ethylene content greater than 50% and insoluble in xylene at room temperature;

(c) 30-60 parts by weight of an amorphous ethylene-propylene copolymer fraction containing optionally small proportions of a diene, soluble in xylene at room temperature and containing 40 to 70% by weight ethylene.

6. The process of claim 5, wherein component (1)(a) is a copolymer of propylene and ethylene containing from 85 to 99% propylene.
7. The process of claim 5, wherein (2)(a) is a propylene homopolymer.
8. The process of claims 5-7 in which prior to irradiation, said linear propylene polymer material is established and maintained in said reduced active oxygen environment.
9. The process of claims 5-7 in which the active oxygen content of said environment is below 0.004% by volume.
10. The process of claims 5-7 or 9 in which the high energy ionizing radiation is an electron beam delivered at a dose rate of 1-10,000 megarads per minute.
11. The process of claims 5-7, 9 or 10 in which the absorbed dose of high energy ionizing radiation is 0.5 to 7 megarads.
12. The process of claims 5-7 in which the period of time of stop (2) is in the range from one minute to one hour, preferably about 2-30 minutes.
13. The process of claims 5-7 in which step (3) is performed by melting the irradiated propylene polymer material.
14. An extrusion coating composition comprising the propylene polymer material of claim 1.
15. A film forming composition comprising the propylene polymer material of claim 1.
16. Film comprising the propylene polymer material of claim 1.
17. A foamed article comprising the propylene polymer material of claim 1.

Patentansprüche

1. Bestrahltes, normalerweise festes, nicht-geradkettiges, im wesentlichen gelfreies Propylenpolymer-Material hohen Molekulargewichts, erhältlich durch das Verfahren gemäß Anspruch 5, mit einer wesentlichen Menge an langen Verzweigungen mit freiem Ende, einer Kaltverfestigungsviskosität beim Dehnen und einer erhöhten Festigkeit der Schmelze, umfassend

(1) eine Propylenpolymer-Zusammensetzung, im wesentlichen bestehend aus:

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(a) 10 bis 50% eines Propylenhomopolymeren mit einem isotaktischen Index von 80-99% oder eines aus der Gruppe ausgewählten Copolymeren, die besteht aus (i) Propylen und Ethylen, (ii) Propylen, Ethylen und einem alpha-Olefin $\text{CH}_2=\text{CHR}$, worin R eine gerad- oder verzweigt-kettige Alkylgruppe mit 2 bis 8 Kohlenstoffatomen bedeutet, und (ii) Propylen und einem alpha-Olefin, wie zuvor in (a) (ii) definiert, wobei das Copolymer 85-99% Propylen enthält und einen isotaktischen Index von mehr als 80 bis 99% besitzt,

(b) 5 bis 20% einer semikristallinen, im wesentlichen geradkettigen Copolymerfraktion mit einer Kristallinität von 20 bis 60%, bestimmt durch Differentialabtauskalorimetrie (DSC), wobei das Copolymer aus der Gruppe ausgewählt ist, die besteht aus (i) Ethylen und Propylen mit einem Gehalt von über 55% Ethylen; (ii) Ethylen, Propylen und einem alpha-Olefin, wie zuvor in (a) (ii) definiert, mit einem Gehalt von 1 bis 10% des alpha-Olefins und über 55% bis zu 98% sowohl Ethylen als auch alpha-Olefin und (ii) Ethylen und einem alpha-Olefin, wie definiert in (a) (ii), mit einem Gehalt von über 55% bis zu 98% dieses alpha-Olefins, wobei das Copolymer bei Raum- oder Umgebungstemperatur in Xylol unlöslich ist, und

(c) 40 bis 80% einer Copolymerfraktion, ausgewählt aus der Gruppe, die besteht aus einem Copolymeren von (i) Ethylen und Propylen, wobei das Copolymer 20% bis weniger als 40% Ethylen enthält (ii) Ethylen, Propylen und einem alpha-Olefin, wie definiert in (a) (ii), wobei das alpha-Olefin in einer Menge von 1 bis 10% vorliegt, und die Menge an Ethylen und die vorliegende Menge an Ethylen und alpha-Olefin 20% bis weniger als 40% beträgt und (iii) Ethylen und einem alpha-Olefin, wie definiert in (a) (ii) mit einem Gehalt von 20 bis weniger als 40% alpha-Olefin und wahlweise mit einem Gehalt an 0,5 bis 10% eines Diens, wobei die Copolymerfraktion in Xylol bei Umgebungstemperatur löslich ist und eine Grenzviskosität von 1,7 bis 3,0 dl/g aufweist, und wobei die Gesamtmenge der Ethyleneinheiten oder der alpha-Olefineinheiten oder der Ethylen- und alpha-Olefineinheiten, falls beide in der Zusammensetzung vorliegen, 15 bis 35% ausmacht, das Gewichtsverhältnis (b)/(c) 0,1 bis etwa 0,3 ist, während der Gesamtgehalt an Ethylen oder C_4 - bis C_8 -alpha-olefin oder deren Kombination in (b+c) weniger als 50% beträgt; oder

(2) eine Propylenpolymer-Zusammensetzung, im wesentlichen bestehend aus:

(a) 10 bis 60 Gewichtsteilen eines homopolymeren Polypropylens mit einem isotaktischen Index von mehr als 90 bis 99, oder eines kristallinen Propylenocopolymeren mit Ethylen mit einem Olefin $\text{CH}_2=\text{CHR}$, worin R ein Alkylrest mit 2 bis 6 Kohlenstoffatomen ist, oder deren Kombinationen, mit einem Gehalt von über 85 Gew.% Propylen und einem isotaktischen Index von mehr als 85 bis 94%;

(b) 8 bis 40 Gewichtsteilen einer kristallinen Polymerfraktion mit einem Gehalt an Ethylen und Propylen und einem Ethylengehalt von mehr als 50%, die in Xylol bei Raumtemperatur unlöslich ist;

(c) 30 bis 60 Gewichtsteilen einer amorphen Ethylen-Propylen-Copolymerfraktion mit einem wahlweisen Gehalt an geringen Mengen eines Diens, die in Xylol bei Raumtemperatur löslich ist und 40 bis 60 Gew. % Ethylen enthält.

2. Propylenpolymer-Material gemäß Anspruch 1, bei dem die Gesamtmenge der Fraktionen (b) und (c), bezogen auf die Olefinpolymer-Gesamtzusammensetzung, 65% bis 80% beträgt.

3. Propylenpolymer-Material gemäß Anspruch 1, bei dem die Komponente (1) (a) ein Copolymer von Propylen und Ethylen mit einem Propylengehalt von 85 bis 99% ist.

4. Propylenpolymermaterial gemäß Anspruch 1, bei dem die Komponente (2) (a) ein Polypropylenhomopolymer ist.

5. Verfahren zur Herstellung eines bestrahlten normalerweise festen, nicht-geradkettigen, im wesentlichen gefahrenen Propylenpolymermaterials hohen Molekulargewichts hoher Kalthärtungsviskosität beim Dehnen aus normalerweise festem, geradkettigen Propylenpolymermaterial hohen Molekulargewichts ohne Kaltverfestigungsviskosität beim Dehnen, umfassend:

(1) Bestrahlen des geradkettigen Propylenpolymer-Materials:

(a) in einer Umgebung, in der die Konzentration an aktivem Sauerstoff auf 15 Vol.% der Umgebung eingestellt und gehalten wird;

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(b) mit ionisierender Strahlung hoher Energie mit einer Dosisrate im Bereich von 1 bis 1×10^4 Megarads, vorzugsweise 18 bis 2.000 Megarads, pro Minute während eines Zeitraums, der ausreicht, daß ein wesentliches Ausmaß einer Kettenspaltung des geradkettigen Propylenpolymeren eintritt, der jedoch unzureichend ist, um ein Gelieren des Materials zu verursachen;

(2) Halten des derart bestrahlten Materials in einer derartigen Umgebung während eines Zeitraums von bis zu einer Stunde; und

(3) anschließende Behandlung des in einer derartigen Umgebung befindlichen bestrahlten Materials, um im wesentlichen sämtliche im bestrahlten Material vorliegenden freien Radikale zu deaktivieren,

bei dem das bestrahlte, normalerweise feste, nichtgeradkettige, im wesentlichen gelfreie Propylenpolymer-Material hohen Molekulargewichts ist:

(1) eine Propylenpolymer-Zusammensetzung, im wesentlichen bestehend aus:

(a) 10 bis 50% eines Propylenhomopolymeren mit einem isotaktischen Index von 80-99% oder eines aus der Gruppe ausgewählten Copolymeren, die besteht aus (i) Propylen und Ethylen, (ii) Propylen, Ethylen und einem alpha-Olefin $\text{CH}_2=\text{CHR}$, worin R eine gerad- oder verzweigt-kettige Alkylgruppe mit 2 bis 8 Kohlenstoffatomen bedeutet, und (iii) Propylen und einem alpha-Olefin, wie zuvor in (a) (ii) definiert, wobei das Copolymer 85-99% Propylen enthält und einen isotaktischen Index von mehr als 80 bis 99% besitzt,

(b) 5 bis 20% einer semikristallinen, im wesentlichen geradkettigen Copolymerfraktion mit einer Kristallinität von 20 bis 60%, bestimmt durch Differentialabwärmekalorimetrie (DSC), wobei das Copolymer aus der Gruppe ausgewählt ist, die besteht aus (i) Ethylen und Propylen mit einem Gehalt von über 55% Ethylen; (ii) Ethylen, Propylen und einem alpha-Olefin, wie zuvor in (a) (ii) definiert, mit einem Gehalt von 1 bis 10% des alpha-Olefins und über 55% bis zu 98% sowohl Ethylen als auch alpha-Olefin und (iii) Ethylen und einem alpha-Olefin, wie definiert in (a) (ii), mit einem Gehalt von über 55% bis zu 98% dieses alpha-Olefins, wobei das Copolymer bei Raum- oder Umgebungstemperatur in Xylol unlöslich ist, und

(c) 40 bis 80% einer Copolymerfraktion, ausgewählt aus der Gruppe, die besteht aus einem Copolymeren von (i) Ethylen und Propylen, wobei das Copolymer 20% bis weniger als 40% Ethylen enthält, (ii) Ethylen, Propylen und einem alpha-Olefin, wie definiert in (a) (ii), wobei das alpha-Olefin in einer Menge von 1 bis 10% vorliegt, und die die vorliegende Menge an Ethylen und alpha-Olefin 20% bis weniger als 40% beträgt und (iii) Ethylen und einem alpha-Olefin, wie definiert in (a) (ii) mit einem Gehalt von 20 bis weniger als 40% alpha-Olefin und wahlweise mit einem Gehalt an 0,5 bis 10% eines Diens, wobei die Copolymerfraktion in Xylol bei Umgebungstemperatur löslich ist und eine Grenzviskosität von 1,7 bis 3,0 dl/g aufweist, und wobei die Gesamtmenge der Ethyleneinheiten oder der alpha-Olefineinheiten oder der Ethylen- und alpha-Olefineinheiten, falls beide in der Zusammensetzung vorliegen, 15 bis 35% ausmacht, das Gewichtsverhältnis (b)/(c) 0,1 bis etwa 0,3 ist, während der Gesamtgehalt an Ethylen oder C_4 - bis C_8 -alpha-olefin oder deren Kombination in (b+c) weniger als 50% beträgt; oder

(2) eine Propylenpolymer-Zusammensetzung, im wesentlichen bestehend aus:

(a) 10 bis 60 Gewichtsteilen eines homopolymeren Polypropylens mit einem isotaktischen Index von mehr als 90 bis 99, oder eines kristallinen Propylen-Copolymeren mit Ethylen, mit einem Olefin $\text{CH}_2=\text{CHR}$, worin R ein Alkylrest mit 2 bis 6 Kohlenstoffatomen ist, oder deren Kombinationen, mit einem Gehalt von über 85 Gew.% Propylen und einem isotaktischen Index von mehr als 85 bis 94%;

(b) 8 bis 40 Gewichtsteilen einer kristallinen Polymerfraktion mit einem Gehalt an Ethylen und Propylen und einem Ethylengehalt von mehr als 50%, die in Xylol bei Raumtemperatur unlöslich ist;

(c) 30 bis 60 Gewichtsteilen einer amorphen Ethylen-Propylen-Copolymerfraktion mit einem wahlweisen Gehalt an geringen Mengen eines Diens, die in Xylol bei Raumtemperatur löslich ist und 40 bis 60 Gew.% Ethylen enthält.

6. Verfahren gemäß Anspruch 5, bei dem die Komponente (1) (a) ein Copolymer von Propylen und Ethylen mit einem Gehalt von 85 bis 99 Propylen ist.

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7. Verfahren gemäß Anspruch 5, bei dem (2) (a) ein Propylenhomopolymer ist.
8. Verfahren gemäß Ansprüchen 5 bis 7, bei dem das geradkettige Propylenpolymer-Material vor der Bestrahlung in die Umgebung mit herabgesetztem aktivem Sauerstoff eingebracht und hierin gehalten wird.
9. Verfahren gemäß Ansprüchen 5 bis 7, bei dem der Gehalt an aktivem Sauerstoff in der Umgebung unterhalb 0,004 Vol.% ist.
10. Verfahren gemäß Ansprüchen 5 bis 7 oder 9, bei dem die ionisierende Strahlung hoher Energie ein mit einer Dosisrate von 1 bis 10.000 Megarads pro Minute abgegebenes Elektronenbündel ist.
11. Verfahren gemäß Ansprüchen 5 bis 7, 9 oder 10, bei dem die absorbierte Dosis der ionisierenden Strahlung hoher Energie 0,5 bis 7 Megarad ist.
12. Verfahren gemäß Ansprüchen 5 bis 7, bei dem der Zeitraum der Stufe (2) im Bereich von 1 Minute bis einer Stunde, vorzugsweise 2 bis 30 Minuten, ist.
13. Verfahren gemäß Ansprüchen 5 bis 7, bei dem die Stufe (3) durchgeführt wird, indem man das bestrahlte Propylenpolymer-Material schmilzt.
14. Extrusionsbeschichtungs-Zusammensetzung, umfassend das Propylenpolymer-Material gemäß Anspruch 1.
15. Filmbildende Zusammensetzung, umfassend das Propylenpolymer-Material gemäß Anspruch 1.
16. Eine Folie, umfassend das Propylenpolymer-Material gemäß Anspruch 1.
17. Geschäumter Gegenstand, umfassend das Propylenpolymer-Material gemäß Anspruch 1.

Revendications

1. Matière de polymère de propylène normalement solide, de poids moléculaire élevé, non linéaire, en grande partie sans gel, susceptible d'être obtenue selon le procédé de la revendication 5 et ayant une quantité importante de longues ramifications à bouts libres, une viscosité d'allongement lors du durcissement par déformation et une résistance augmentée à l'état fondu comprenant :

(1) une composition de polymère de propylène constituée essentiellement de :

- (a) 10 à 50% d'homopolymère de propylène ayant un indice isotactique de 80 à 99%, ou un copolymère choisi parmi le groupe constitué d'un copolymère de (i) propylène et éthylène, (ii) propylène, éthylène et une alpha-oléfine $\text{CH}_2 = \text{CHR}$, où R est un alcoyle à chaîne droite ou ramifiée en C_{2-8} et (iii) propylène et une alpha-oléfine, comme défini ci-dessus en (a) (ii), où ledit copolymère contient 85 à 99% de propylène et ayant un indice isotactique plus grand que 80 à 99%,
- (b) 5 à 20% d'une fraction de copolymère semi-cristallin, essentiellement linéaire, ayant une cristallinité de 20 à 60%, par calorimétrie par analyse différentielle (DSC), où le copolymère est choisi parmi le groupe constitué d'un copolymère de (i) éthylène et propylène contenant plus de 55% d'éthylène; (ii) éthylène, propylène et une alpha-oléfine comme défini ci-dessus en (a) (ii), contenant 1 à 10% de l'alpha-oléfine et plus de 55% jusqu'à 98% d'éthylène et d'alpha-oléfine ensemble; et (iii) éthylène et une alpha-oléfine comme défini en (a) (ii), contenant plus de 55% jusqu'à 98% de ladite alpha-oléfine, ce copolymère étant insoluble dans le xylène à température de la pièce ou ambiante, et
- (c) 40 à 80% d'une fraction de copolymère choisi parmi le groupe constitué d'un copolymère de (i) éthylène et propylène où le copolymère contient 20% à moins de 40% d'éthylène; (ii) éthylène, propylène et une alpha-oléfine comme défini ci-dessus en (a) (ii), où l'alpha-oléfine est présente dans une quantité de 1 à 10% et la quantité d'éthylène et d'alpha-oléfine présente est de 20% à moins de 40%; et (iii) éthylène et une alpha-oléfine, comme défini en (a) (ii), contenant de 20 à moins de 40% d'alpha-oléfine, et facultativement contenant 0,5 à 10% d'un diène, ladite fraction de copolymère étant soluble dans le xylène à température ambiante et ayant une viscosité intrinsèque de 1,7 à 3,0 dl/g, où la quantité totale d'unités d'éthylène ou desdites unités d'alpha-oléfine ou d'éthylène et desdites unités d'alpha-oléfine quand elles

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sont présentes ensemble dans la composition est de 15 à 35%, le rapport en poids de (b)/(c) est de 0,1 à environ 0,3 et la teneur totale d'éthylène ou d'alpha-oléfine en C₄₋₈ ou de combinaison de celles-ci dans (b + c) est inférieur à 50%; ou

5 (2) une composition de polymère de propylène constituée essentiellement de :

(a) 10-60 parties en poids de polypropylène homopolymère avec un indice isotactique plus grand que 90 à 99, ou d'un copolymère de propylène cristallin avec de l'éthylène, avec une oléfine CH₂ = CHR où R est un radical alcoyle de 2-6 carbones, ou des combinaisons de ceux-ci, contenant plus de 85% en poids de propylène et ayant un indice isotactique plus grand que 85 à 94%;

10 (b) 8-40 parties d'une fraction de polymère cristallin contenant de l'éthylène et du propylène, ayant une teneur en éthylène plus grande que 50% et insoluble dans le xylène à température ambiante;

15 (c) 30-60 parties en poids d'une fraction de copolymère amorphe d'éthylène-propylène contenant facultativement des petites proportions d'un diène, soluble dans le xylène à température ambiante et contenant 40 à 70% en poids d'éthylène.

2. Matière de polymère de propylène selon la revendication 1, où la quantité totale des fractions (b) et (c) par rapport à la composition totale de polymère d'oléfine est de 65% à 80%.

20 3. Matière de polymère de propylène selon la revendication 1, où le composant (1) (a) est un copolymère de propylène et d'éthylène contenant 85% à 99% de propylène.

4. Matière de polymère de propylène selon la revendication 1, où le composant (2) (a) est un homopolymère de polypropylène.

25 5. Procédé de fabrication d'une matière de polymère de propylène irradiée, normalement solide, de poids moléculaire élevé, non linéaire, en grande partie sans gel, avec une viscosité d'allongement lors du durcissement par déformation à partir d'une matière de polymère de propylène, normalement solide, de poids moléculaire élevé, linéaire, sans viscosité d'allongement lors du durcissement par déformation qui comprend :

30 (1) l'irradiation de ladite matière de polymère de propylène, linéaire

(a) dans un environnement dans lequel la concentration en oxygène actif est établie et maintenue à moins de 15% en volume dudit environnement;

35 (b) avec une radiation ionisante de haute énergie à un débit de dose dans l'intervalle de 1 à 1×10^4 mégarads, de préférence 18-2 000 mégarads, par minute pendant une période de temps suffisante pour qu'une quantité importante de scission de la chaîne du polymère de propylène linéaire apparaisse mais insuffisante pour provoquer la solidification de la matière;

40 (2) le maintien de la matière ainsi irradiée dans cet environnement pendant une période de temps allant jusqu'à une heure; et

(3) ensuite le traitement de la matière irradiée quelque temps dans cet environnement pour désactiver en grande partie tous les radicaux libres dans la matière irradiée, dans laquelle ladite matière de polymère de propylène irradiée, normalement solide, de poids moléculaire élevé, non linéaire, en grande partie sans gel est constituée de :

45 (1) une composition de polymère de propylène constituée essentiellement de :

50 (a) 10 à 50% d'un homopolymère de propylène, ayant un indice isotactique de 80 à 99%, ou un copolymère choisi parmi le groupe constitué d'un copolymère de (i) propylène et éthylène, (ii) propylène, éthylène et une alpha-oléfine CH₂ = CHR, où R est un alcoyle en chaîne droite ou ramifiée en C₂₋₈, et (iii) propylène et une alpha-oléfine, comme défini ci-dessus en (a) (ii), où ledit copolymère contient 85 à 99% de propylène et ayant un indice isotactique plus grand que 80 à 99%;

55 (b) 5 à 20% d'une fraction de copolymère semi-cristallin, essentiellement linéaire, ayant une cristallinité de 20 à 60%, par calorimétrie par analyse différentielle (DSC), où le copolymère est choisi parmi le groupe constitué d'un copolymère de (i) éthylène et propylène contenant plus de 55% d'éthylène; (ii) éthylène, propylène et une alpha-oléfine comme défini ci-dessus en (a) (ii), contenant de 1 à 10% de l'alpha-oléfine et plus de 55% jusqu'à 98% d'éthylène et d'alpha-oléfine ensemble; et (iii) éthylène et une alpha-oléfine

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comme défini en (a) (ii), contenant plus de 55% jusqu'à 98% de ladite alpha-oléfine, ce copolymère étant insoluble dans le xylène à température de la pièce ou ambiante, et

(c) 40 à 80% d'une fraction de copolymère, choisi parmi le groupe constitué d'un copolymère de (i) éthylène et propylène où le copolymère contient 20% à moins de 40% d'éthylène; (ii) éthylène, propylène et une alpha-oléfine comme défini ci-dessus en (a)(ii), où l'alpha-oléfine est présente dans une quantité de 1 à 10%, et la quantité d'éthylène et d'alpha-oléfine présente est de 20% à moins de 40%; et (iii) éthylène et une alpha-oléfine, comme défini en (a) (ii), contenant de 20 à moins de 40% d'alpha-oléfine, et facultativement contenant 0,5 à 10%, de préférence 1 à 5% d'un diène, ladite fraction de copolymère étant soluble dans le xylène à température ambiante et ayant une viscosité intrinsèque de 1,7 à 3,0 dl/g, où la quantité totale des unités d'éthylène ou desdites unités d'alpha-oléfine ou d'éthylène et desdites unités d'alpha-oléfine quand elles sont présentes ensemble dans la composition est de 15 à 35%, le rapport en poids de (b)/(c) est de 0,1 à environ 0,3 et la teneur totale d'éthylène ou d'alpha-oléfine en C₄₋₈ ou de combinaison de celles-ci dans (b + c) est inférieure à 50%; ou

(2) une composition de polymère de propylène constituée essentiellement de :

(a) 10-60 parties en poids de polypropylène homopolymère avec un indice isotactique plus grand que 90 à 99, ou d'un copolymère de propylène cristallin avec de l'éthylène, avec une oléfine CH₂ = CHR où R est un radical alcoyle de 2-6 carbones, ou des combinaisons de ceux-ci, contenant plus de 85% en poids de propylène et ayant un indice isotactique plus grand que 85 à 94%;

(b) 8-40 parties d'une fraction de polymère cristallin contenant de l'éthylène et du propylène, ayant une teneur en éthylène plus grande que 50% et insoluble dans le xylène à température ambiante;

(c) 30-60 parties en poids d'une fraction de copolymère amorphe d'éthylène-propylène contenant facultativement des petites proportions d'un diène, soluble dans le xylène à température ambiante et contenant 40 à 70% en poids d'éthylène.

6. Procédé selon la revendication 5, dans lequel le composant (1)(a) est un copolymère de propylène et d'éthylène contenant 85% à 99% de propylène.

7. Procédé selon la revendication 5, dans lequel (2)(a) est un homopolymère de propylène.

8. Procédé selon les revendications 5-7 dans lequel avant l'irradiation, ladite matière de polymère de propylène linéaire est établie et maintenue dans ledit environnement à oxygène actif réduit.

9. Procédé selon les revendications 5-7 dans lequel la teneur en oxygène actif dudit environnement est inférieure à 0,004% en volume.

10. Procédé selon les revendications 5-7 ou 9 dans lequel la radiation ionisante de haute énergie est un faisceau d'électrons libéré à un débit de dose de 1-10 000 mégarads par minute.

11. Procédé selon les revendications 5-7, 9 ou 10 dans lequel la dose absorbée de la radiation ionisante de haute énergie est de 0,5 à 7 mégarads.

12. Procédé selon les revendications 5-7 dans lequel la période de temps de l'étape (2) est dans l'intervalle d'une minute à une heure, de préférence environ 2-30 minutes.

13. Procédé selon les revendications 5-7 dans lequel l'étape (3) est effectuée en faisant fondre la matière de polymère de propylène irradiée.

14. Composition de couchage par extrusion comprenant la matière de polymère de propylène selon la revendication 1.

15. Composition formant un film comprenant la matière de polymère de propylène selon la revendication 1.

16. Film comprenant la matière de polymère de propylène selon la revendication 1.

17. Article expansé comprenant la matière de polymère de propylène selon la revendication 1.

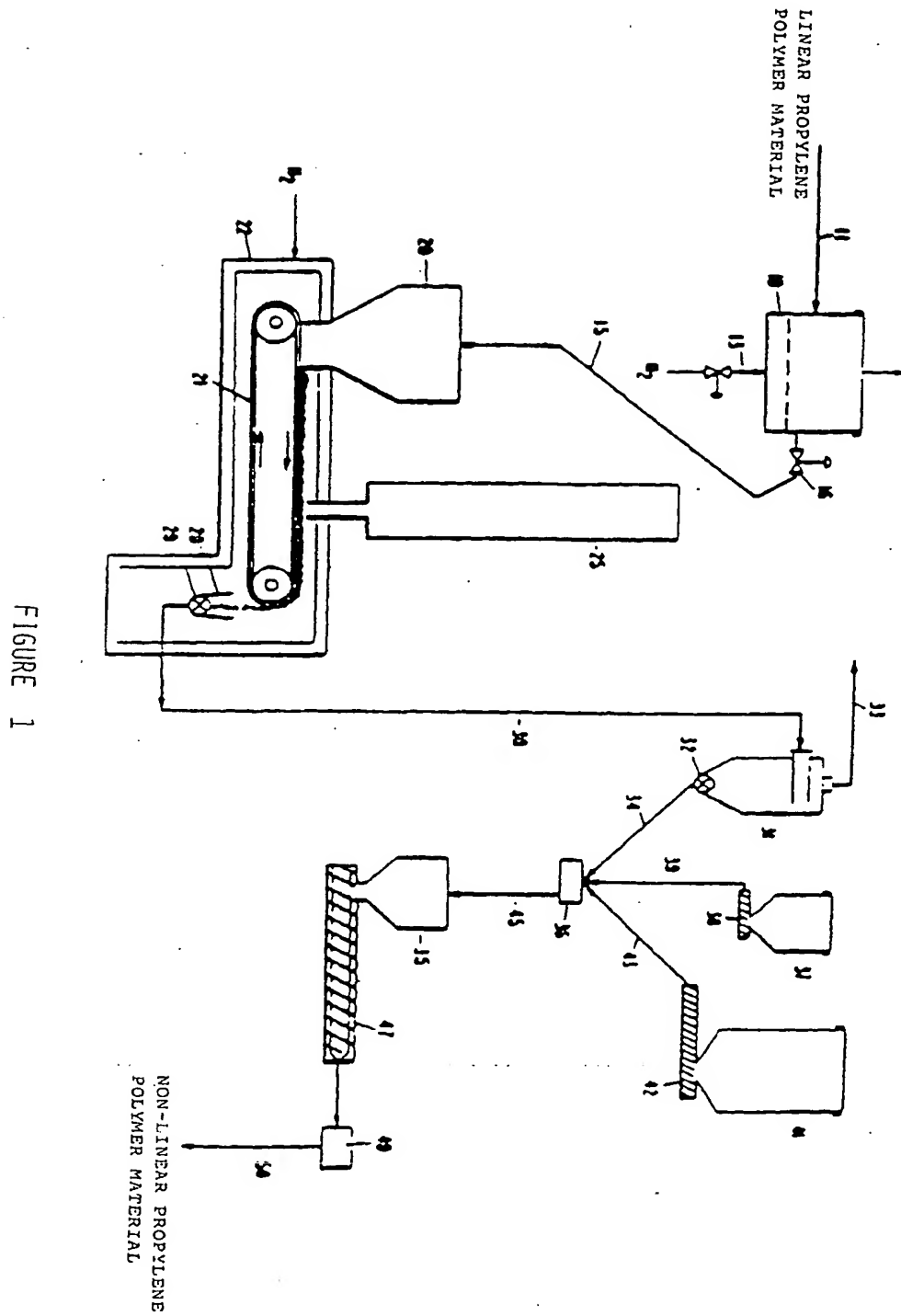


FIGURE 1

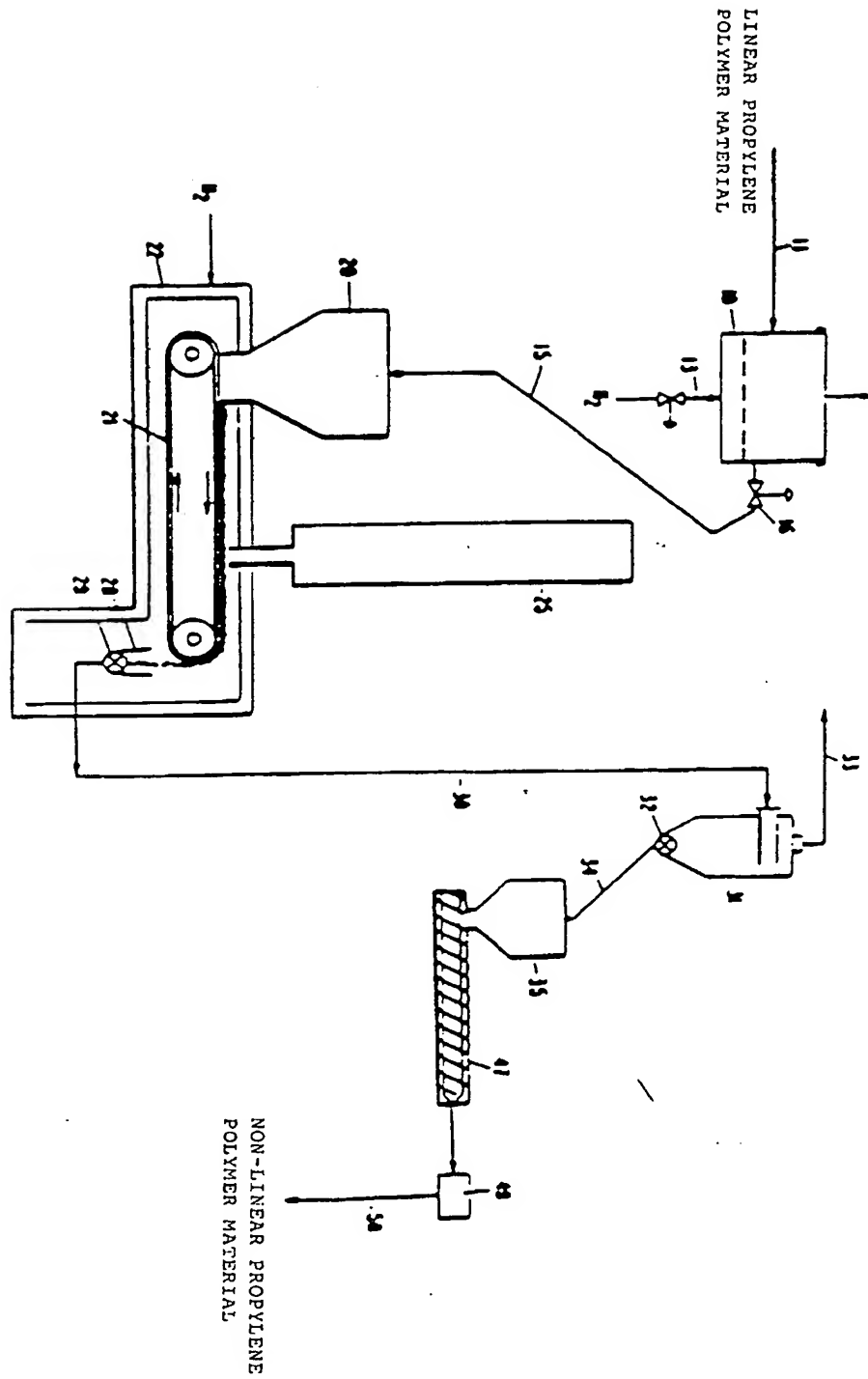


FIGURE 2